SoRI-EAS-86-107

FABRICATION AND EVALUATION OF ETHANOL-SELECTIVE MEMBRANES

Final Progress Report

to

SOLAR ENERGY RESEARCH INSTITUTE
1617 Cole Boulevard
Golden, CO 86401

Contract XX-4-04135-1

SOUTHERN RESEARCH INSTITUTE
2000 Ninth Avenue South
P.O. Box 55305
Birmingham, AL 35255-5305

January 31, 1986
Project 5700-XII/F

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FABRICATION AND EVALUATION OF ETHANOL-SELECTIVE MEMBRANES

I. INTRODUCTION

The separation of ethanol from water is an energy-intensive step in the production of ethanol from biomass. If conventional distilllation is used, the energy requirements for product recovery can exceed 20% of the heating value of the ethanol (1). This figure can be reduced by the use of various internal-heat recovery schemes such as vapor recompression. Unfortunately, systems of this type are quite expensive and significantly increase the capital costs for the product recovery.

In recent years, a variety of alternative separation processes have been investigated that hold considerable promise for reducing the energy and capital costs associated with ethanol purification. A membrane process, pervaporation, appears to be one of the most promising alternatives. In pervaporation, feed solution flows as a thin film across the upstream surface of a membrane. Material that permeates the membrane is continuously removed as vapor from the downstream surface. The composition of the permeate depends not only on the composition of the feed solution but also on the relative permeabilities of the individual components in the membrane. By proper selection of the membrane material, the vapor/liquid equilibrium across the membrane can be shifted, and the product can be either the permeate or the retentate. Moreover, azeotropes that limit product purity in conventional distillation can be overcome.

In principle, it is possible to replace the entire distillation section of an alcohol plant with pervaporation membranes. Pervaporation membranes are, however, highly susceptible to fouling by undissolved material such as those present in fermentation beers. Consequently, it is unlikely that a fermentation beer can be fed directly to a pervaporation unit without an initial clarification step. The clarification step can be accomplished by either simple distillation or ultrafiltration.

The product of the clarification step will be fed to either an ethanol-selective or water-selective membrane, depending on the concentration of ethanol in the clarified stream. In general, it is desirable to use a membrane that is selective for the minor constituent of the feed stream to minimize the permeate volume and the total energy required for the separation. Ethanol-selective membranes are desirable when the ethanol concentration in the feed is low, and water-selective membranes are desirable when the ethanol concentration is high. In either case, the permeate stream may contain considerable energy that will need to be recovered to avoid excessive energy losses for the overall process. Because the permeate stream is a low-temperature, low-pressure vapor, the capital cost for heat recovery may be quite high. The optimum system will represent a balance between the energy and capital costs for the overall process.

Various investigators (2-8) have studied the separation of aqueous ethanol solutions by pervaporation, and a variety of processes using distillation or ultrafiltration in conjunction with ethanol- and water-selective membranes have been proposed. Almost no work has been reported in the open literature, however, on the economics of ethanol recovery by pervaporation.

As a major part of this project, we conducted an economic analysis of the capital and energy costs for dehydration of aqueous ethanol solutions by both distillation and pervaporation. This work was done to establish performance criteria for the further development of pervaporation membranes. The analysis was based on an annual production of 95,000,000 liters (25,000,000 gallons per year) of 99.9$^+$% ethanol from an 8.5 wt % beer. The costs include storage and transfer of the fermentation beer, purification, and waste treatment. For comparison, the capital and energy costs for an azeotropic distillation using benzene have been included. Three processes that use pervaporation membranes are described. The membrane areas and estimated cost of the installed membranes for each process are also presented.

The remaining effort on this project involved the fabrication and evaluation of membranes. Initially, we directed our efforts toward the development of ethanol-selective membranes. The results of the economic evaluation showed that the use of ethanol-selective membranes in the purification of ethanol from fermentation beers was not economically reasonable in light of the low capital and energy costs for simple distillation in the lower ethanol-concentration ranges. For this reason, we redirected our effort during the last few months of the project toward the development of water-selective membranes. The results of our studies are described in the following sections.

II. LITERATURE REVIEW

We conducted an intensive literature review for information on pervaporation and the use of membranes in ethanol purification. Although numerous references were identified, only a few were useful for our studies. Table 1 summarizes the data from the most significant papers (1-8) concerning separation of aqueous ethanol solutions by pervaporation. The flux data were taken directly from the references without normalizing for membrane thickness. Most of the work has involved the use of glassy polymers in the form of either homogeneous, composite, or anisotropic membranes. The most extensive survey of polymer types is that of Smolders et al. (5). Schissel and Orth (7) studied the effect of temperature on selectivity and flux for several commercial porous

TABLE 1. SUMMARY OF MEMBRANE FLUX AND SELECTIVITY FOR SELECTED PERVAPORATION DATA

Membrane[a]	Feed composition, wt % ethanol	$\alpha_{EtOH}^{H_2O}$ [b]	T, °C	J,[c] cm/h	Reference
Cellophane	50	0.9	25	0.10	1
Cellophane	50	9.0	30	0.13	1
Cellophane	50	2.0	45	0.46	2
Cellophane	90.1	8.0	60	0.30	3
Cellulose	96	6.2	20	0.01	4
Cellulose acetate (A)	50	1.0	20	0.325	5
Cellulose acetate	50	2.0	20	0.113	5
Cellulose acetate	50	3.9	20	0.065	5
Cellulose acetate	50	4.2	20	0.068	5
Cellulose acetate (A)	50	5.9	20	0.042	5
Cellulose acetate (A)	50	12.3	20	0.027	5
Cellulose acetate	55	8.5	80	0.20	6
Cellulose acetate (A)	93.5	1.4	23	1.34	7
Cellulose acetate (A)	93.5	2.8	33	0.28	7
Cellulose acetate (A)	93.5	3.5	43	0.24	7
Cellulose acetate	96	11	60	0.05	3
Cellulose triacetate	50	2.7	20	0.089	5
Cellulose triacetate	50	36	20	0.023	5
Cellulose acetate butyrate	50	3.2	20	0.023	5
Cellulose acetate butyrate	50	4.0	20	0.042	5
Cellulose acetate butyrate	50	4.1	20	0.033	5

(continued)

TABLE 1 (continued)

Membrane[a]	Feed composition, wt % ethanol	$\alpha^{H_2O}_{EtOH}$[b]	T, °C	J,[c] cm/h	Reference
Cellulose acetate butyrate	50	9.6	20	0.029	5
Cellulose tripropionate	50	2.6	20	0.055	5
Polyacrylonitrile	50	70	20	0.0015	5
PAN/Nylon 6 (C)	50	9	20	0.0015	5
Polysulfone (A)	50	75	20	0.014	5
Polysulfone (A)	50	332	20	0.0004	5
PSF/PVDF (C)	50	19	20	0.005	5
Nylon 6 Support	50	1.0	20	--	5
PVDF Support	50	1.0	20	0.20	5
PVDF	50	1.0	20	0.045	5
Polyetherurea	93.7	1.4	23	1.3	7
Polyetherurea	93.6	3.7	33	0.2	7
Polyetherurea	93.5	14.8	43	0.06	7
Polyetherurea	93.5	10.0	53	0.09	7
Polyetherurea	92.0	2.6	23	0.09	7
Polyetherurea	92.3	13.9	33	0.05	7
Polyetherurea	92.4	8.2	43	0.05	7
Polyetherurea	45.2	0.3	23	0.31	7
Polyetherurea	44.9	0.4	33	0.66	7
Polyetherurea	45.3	0.4	43	0.94	7

(continued)

TABLE 1 (continued)

Membrane[a]	Feed composition, wt % ethanol	$\alpha_{EtOH}^{H_2O}$[b]	T, °C	J,[c] cm/h	Reference
Polyetherurea	92.2	4.2	43	0.15	7
Polyetherurea	92.5	13.3	43	0.07	7
Polyetherurea	95.8	8.8	43	0.11	7
Polyetherurea	2.8	0.3	43	0.54	7
Polyetherurea	1.4	0.35	43	0.57	7
Polyetherurea	0.9	0.4	43	0.86	7
Polyphenyleneoxide (A)	50	1.0	20	0.192	5
Polyphenyleneoxide (A)	50	9.3	20	0.002	5
Polydimethylsiloxane	5	0.3	20	0.017	5
Polydimethylsiloxane	50	0.22	20	0.019	5

[a] (A) = Asymmetric, (C) = Composite
[b] α = Selectivity
[c] J = Flux

membranes. Aside from the work of Schissel and Orth, the effect of feed composition on selectivity has not been studied in detail.

These data were used for two purposes in our work. First, the data were used as input data for the cost estimates of purification by pervaporation. Second, the data were used to aid in selecting materials for use in our experimental work.

III. ECONOMIC EVALUATION

In our economic evaluation, we considered the capital and energy costs for purifying an 8.5% ethanol beer to a $99.5^{+}\%$ ethanol product with an annual plant capacity of 95,000,000 L. The evaluation takes into account storage and transfer of the fermentation product, purification, and waste treatment. The cost estimates presented in the following sections were prepared by standard cost-estimating techniques based on conceptual designs. In this method of estimating, the purchased costs of the individual pieces of equipment are either obtained by quotations or are taken for the proper sizes of equipment from published cost information. The sizes of the equipment were calculated from material balances and from residence times and rates. The costs for individual items were updated from the base year given in the publications to 1985 by multiplying them by the ratio of the Marshall and Swift plant equipment cost index (MS Index) for 1985 to the MS Index for the base year.

The 1985 purchased costs of the individual items for each section are summed, and the installed cost of the equipment in that section is found by multiplying by the so-called "Lang factor" for the type of operation involved (solids processing, fluid-solids processing, or fluid processing). These Lang factors include the costs of field material and labor; the cost of installation including foundations, erection, and setting of equipment; the costs for insulation, painting, piping, instrumentation, and electrical facilities; and the indirect costs, such as freight, insurance, taxes, construction overhead, engineering, contractor's fee, and contingencies. The Lang factors for the various types of operation are solids processing, 3.51; fluid-solids processing, 3.63; and fluid processing, 4.72.

Estimates for three purification processes involving membranes have been determined. These are presented along with cost summaries for performing the separation by distillation alone. The four processes considered for evaluation were:

Case I. Azeotropic distillation.

Case II. Distillation to 80 wt % ethanol followed by dehydration using water-selective membranes.

Case III. Distillation to 40 wt % ethanol and then concentration by ethanol-selective membranes to 80 wt % ethanol followed by water-selective membranes.

Case IV. Ultrafiltration followed by exposure to ethanol-selective membranes to produce 80 wt % ethanol and then dehydration by water-selective membranes.

A. Storage and Transfer

The following equipment is for temporary storage and transfer of the fermentation product between the fermentors and the distillation units. The size, cost, and method of cost estimation are given for each item. Costs for purchased and installed equipment are summarized in Table 2.

1. Beer wells

These receive the 8.5% beer from the fermentors and are large enough to store beer produced in 8 h (1,022,000 L) for a 95,000,000-L/yr production of 99.5+% ethanol product. To provide some free volume, we assume the use of two 562,500-L, low-carbon-steel tanks built to API standards. The costs of these were taken from an article in "Modern Cost Engineering Methods and Data" by the staff of Chemical Engineering Magazine. The cost data in the article were dated in 1978. We updated the cost to January 1985 by the ratio of the Marshall and Stevens plant equipment cost index (MS index) for 1985 (787) to that index for 1978 (545). The updated purchased cost for both tanks is $92,400.

2. Beer-transfer pump

This pump is used to transfer the beer to the proper plate of the beer still in the ethanol-distillation section. The pump must transfer 2140 L/min. The 1976 cost from the Modern Cost Engineering reference was $1750. The cost included the cost of the pump, base plate, V-belt drive, motor, and foundation. This cost was updated by the ratio of the 1985 MS index (787) to that in 1976 (472). The updated cost was $2900.

B. Distillation--Case I

The costs for three distillation systems are summarized in Table 3. The systems include two azeotropic distillation processes and one vapor reuse process. Three systems are presented to demonstrate the range of capital costs and energy requirements that can be obtained depending on the assumptions used in preparing the cost estimates. The first azeotropic process is based on an estimate obtained from Glitsch Engineering (West Caldwell, NJ) in December

TABLE 2. PURCHASED EQUIPMENT COSTS FOR DISTILLATION SECTION

Item	Cost, $	Energy Cost, kJ/ℓ
Storage and transfer		
Beer wells	92,400	0
Beer-transfer pump	2,900	37.35
Subtotal	95,300	
Installed cost using Lang factor[a]	449,816	
Subtotal for storage and transfer	449,816	37.35
Distillation		
Ethanol-stillage pump	2,900	2.48
Ethanol-product pump	2,100	2.48
Ethanol-storage tank	99,400	0
Steam boiler	175,000	8586.57[b]
Subtotal	279,400	
Installed cost using Lang factor[a]	1,318,768	
Turnkey ethanol-distillation unit	2,113,000	157.68
Subtotal for distillation	3,431,768	8744.25
Total	3,881,584	8781.60

[a] Lang factor for fluid processing is 4.72.

[b] Energy costs are based on a generator efficiency of 60%.

TABLE 3. SUMMARY OF CAPITAL AND ENERGY COSTS FOR DISTILLATION SEPARATION--CASE I

System	Concentration, wt %	Installed equipment cost, $ x 10⁶	Energy requirement,[a] kcal/kg
Azeotropic distillation[b]	8.5 - 99.5	3.4	2,285 (27,000)
Azeotropic distillation[c]	7.1 - 99.5	4.9	1,840 (21,700)
Vapor reuse distillation[d]	10 - 99.9	2.8	1,520 (18,000)

[a] Numbers in parentheses are Btu/gal.

[b] Glitsch Engineering, Caldwell, NJ.

[c] A Guide to Commercial-Scale Ethanol Production and Financing; SERI/SP-751-877: 1980.

[d] Evaluation of Nondistillation Ethanol Separation Processes; SERI/TR-231-1887: 1983.

1983 of $1,000,000 for a complete turnkey ethanol-distillation section producing 28,125,000 L/yr of $99.5^{+}\%$ ethanol product. The overhead product is removed as vapor, condensed, and stored in tanks designed to hold one week's production of ethanol. The installed cost is given in 1985 dollars as updated by multiplying the base-year cost by the ratio of the MS plant equipment cost index for the base year. The other two distillation processes were taken from SERI reports and are included for comparison only.

Units included in the Glitsch Engineering estimate are a beer still, an azeotropic-distillation column, a column to separate the azeotropic agent (benzene) and the ethanol, the necessary transfer pumps, interstage storage tanks, and a recycle circuit for the azeotropic agent. The size, cost, and method of cost estimation for each item are provided in the following sections and are summarized in Table 2.

1. Distillation unit

We first estimated the 1983 cost of a similar turnkey ethanol section to produce 95,000,000 L/yr by the usual Chemical Engineering 0.6 factor (i.e., $[(95{,}000{,}000)/(28{,}125{,}000)]^{0.6}$ x cost for 28,125,000-L/yr plant). We then updated the cost from 1983 to 1985 by the ratio of the MS indices. The updated cost for a 95,000,000-L/yr plant is $2,113,000.

2. Ethanol-stillage pump

Because the rate of stillage production was only slightly less than the rate of feed to the still, we assumed the same size pump. The 1985 cost is $2900.

3. Ethanol-product storage tank

We assumed storage for a 1-week supply of $99.5^{+}\%$ product (1,800,000 L). A 1,800,000-L tank of low-carbon steel fabricated to API standards was assumed. From the Modern Cost Estimating reference, the 1978 cost was $68,810. The 1985 cost is $99,400.

4. Ethanol-product pump

The pump assumed for use would deliver 150 L/min. From Modern Cost Engineering, the cost in 1976 was $1250. When this is updated to 1985 by the ratio of MS indices (787/472), the updated cost is $2100.

5. Steam boiler

For a 95,000,000-L/yr ethanol-distillation plant, 22,750 kg/h of 250-psi steam will be needed as estimated from the steam requirement for a 28,125,000-L/yr plant given in the Glitsch Engineering estimate. The cost of a 22,750-kg/h packaged steam boiler in 1969 was taken from Modern Cost Estimating

Techniques (8). The cost in 1969 was $60,000. The cost includes an oil-fired boiler, fans, instruments and controls, burners, sootblowers, feed pumps, deaerators, chemical-injection system, stack, and assembly. The 1985 cost was estimated by applying the ratio of the 1985 MS index (787) to that for 1969 (269). The estimated cost in 1985 is $175,000.

C. Pervaporation--Cases II, III, and IV

To estimate the cost of separating aqueous ethanol solutions by pervaporation, it is necessary to estimate first the membrane areas for the proposed process. The following paragraphs describe the calculations used to estimate membrane areas, retentate flow and composition, product flow and composition, stage area, and the temperature drop in a pervaporation unit.

In a pervaporation unit, feed solution flows as a thin film across one surface (the upstream surface) of a membrane. Vacuum is applied to the other surface (the downstream surface), and material that permeates the membrane is continuously removed as vapor. The product may be either the retentate stream or the permeate stream, depending on the selectivity of the membrane used. To determine the flow rates and compositions of the various streams, we began by performing a material balance over the pervaporation unit.

A material balance performed over the pervaporation unit for component "a" (highly permeable species) gives:

$$F(x_a)_f = R\,(x_a)_r + P(y_a) \tag{1}$$

where

F = feed rate, mole/s

R = retentate, mole/s

P = permeate, mole/s

x_a = mole fraction of component a in the liquid phase

y_a = mole fraction of component a in the vapor phase

Let

θ = mole fraction of the feed in the permeate

Then Equation 1 becomes:

$$F(x_a)_f = (1 - \theta)F(x_a)_r + \theta F(y_a) \tag{2}$$

Equation (2) contains three unknowns: θ, $(x_a)_r$, and (y_a). The mole fraction (y_a) can be determined by the selectivity factor α, which is based on the characteristics of the membrane being used in the pervaporation unit.

By definition, the selectivity factor is equal to the ratio of the mole fractions in the permeate divided by the ratio of mole fractions in the feed, which are known values. Selectivity can be expressed mathematically

$$\alpha_b^a = \frac{(y_a/y_b)}{(x_a/x_b)_f} \tag{3}$$

Substituting in $y_b = 1 - y_a$ gives:

$$\alpha_b^a = \frac{y_a/[1 - (y_a)]}{(x_a/x_b)_f} \tag{4}$$

Rearranging,

$$\alpha_b^a(x_a/x_b)_f[1 - (y_a)] = (y_a) \tag{5}$$

$$\alpha_b^a(x_a/x_b)_f = \alpha_b^a\ (x_a/x_b)_f(y_a) + (y_a) \tag{6}$$

$$\alpha_b^a(x_a/x_b)_f = [\alpha_b^a(x_a/x_b)_f + 1](y_a) \tag{7}$$

Finally solving for y_a:

$$(y_a) = \frac{\alpha_b^a(x_a/x_b)_f}{1 + \alpha_b^a(x_a/x_b)_f} \tag{8}$$

By definition, the permeability of a liquid through a membrane is described mathematically by the following equation:

$$Q_i = \frac{J_i^m \ell}{\Delta P} = \frac{J_i^m \ell}{P_i^0(x_i - P_{ri}y_i)} \tag{9}$$

where

P_{ri} = generalized pressure ratio $\frac{P_2\phi_i}{P_i\gamma_i}$

Q_i = permeability coefficient of component i, $\frac{\text{mole} \cdot \text{cm}}{\text{s} \cdot \text{dyne}}$

J_i = molar flux of component i in the membrane, $\frac{\text{mole}}{(\text{cm}^2 \cdot \text{s})}$

ℓ = membrane thickness, cm

P_i^0 = vapor pressure of pure component i at system conditions, dyne/cm^2

P_2 = pressure in the vapor side of the pervaporation unit, dyne/cm^2

ϕ = fugacity coefficient of component i in the vapor phase

γ = activity coefficient of component i in the liquid phase

Assuming a vacuum exists on the vapor side of the pervaporation unit, the pressure on the vapor side is approximately equal to zero; thus, $P_2 \cong 0$. This changes the permeability equation in terms of "a" to:

$$Q_a = \frac{J_a \ell}{P_a^0 (x_a)_r} \tag{10}$$

By definition, the molar flux, J_a, is equal to the flow rate of the permeate divided by the area of the membrane, S, or mathematically:

$$J_a = \frac{\Theta F(y_a)}{S} \tag{11}$$

The molar flux can also be expressed as a function of permeation rate:

$$J_a = \frac{(r_p)(\rho_a)}{MW} \tag{12}$$

where

r_p = permeation rate, cm/s

ρ_a = density of component a, g/cm^3

MW = molecular weight, g/mole

Substitution of Equation (11) into Equation (12) and solving for S gives:

$$S = \frac{\Theta F(y_a)MW}{(r_p)(\rho_a)} \qquad (13)$$

The only unknown on the right side of the equation is Θ, the fraction of the feed in the permeate. Equation (13) can be solved by picking Θ and calculating S, the area required for the separation.

The equation developed above to calculate the required area applies to separations where the concentration of the liquid is assumed to be constant along the length of the membrane. To make this assumption, it must also be assumed that the liquid phase is completely mixed (i.e., no boundary-layer effects are taken into consideration). Under complete mixing conditions, the separation factor becomes identical with the ideal separation factor. Therefore, Equation (13) would apply only to an ideal separation. The model also assumes that the separation factor is not concentration dependent and, therefore, is the same for all stages in the separation. It should also be noted that the effect of temperature on the selectivity and flux of the membrane has been ignored. The effects of boundary-layer resistance and the temperature dependence of the flux and selectivity were ignored in our calculations because no reliable data could be found from which to estimate the magnitudes of these factors.

From these equations, we designed a computer program to calculate the area required for a given separation. A stage area of 0.01 m^2 is assumed, and the amount of separation that will occur with that stage is calculated. The program then proceeds in a stagewise fashion, adjusting the feed rate and composition for each successive stage to the rate and composition of the retentate stream from the previous stage and assuming an area of 0.01 m^2 each time. After each stage, the program compares the product composition to the test composition. When the test composition is reached, the areas from each stage are summed to give the total area required for the separation. Likewise, the permeate flows are summed to determine the amount and composition of the permeant stream.

The following input data are required for determining the required areas:

- selectivity of ethanol over water, α_w^e
- selectivity of water over ethanol, α_e^w
- permeation rate, cm/h
- membrane thickness, cm
- assumed membrane thickness, cm
- feed rate, ℓ/h
- density, g/cm^3
- mole fraction of feed
- desired product composition
- feed temperature

Output data:

- retentate product rate, g/h
- permeate product rate, g/h
- retentate composition
- permeate composition
- membrane area, m^2
- stage area
- temperature cycle
- energy demand

As a first step in the estimation of purification costs for pervaporation, we calculated the required membrane areas for experimental membranes reported in the literature. The selectivity factor and the permeation rate were taken from literature data. By decreasing the thickness of the membrane, the separation process will require less area. For this reason, an assumed permeation rate was calculated based on the ratio of the actual thickness to an assumed thickness (i.e., the minimum thickness that we think can be achieved). The desired product composition specifies the amount of ethanol in the product stream. The product stream is the permeate for an ethanol-selective membrane and the retentate for a water-selective membrane. Next, we calculated the required areas for a number of hypothetical membranes exhibiting higher values of flux and selectivity than those reported in the literature.

After calculating the membrane areas for several of the cases presented in the following sections, we calculated the energy requirements for the pervaporation section using published enthalpy data (9). These calculations showed that, in every case, the temperature drop of the feed stream was too great to allow the separation to be achieved in a single pervaporation unit. Consequently, the separation must be done in stages with reheating of the feed between stages in the cascade. We then modified our program to allow the number of stages in the cascade to be input and to calculate the energy consumption, energy requirement, and the temperature drop across each stage. These results are presented in the following sections.

1. Case II

This process involves distillation to 80 wt % ethanol followed by dehydration using water-selective membranes. A block diagram for this process is shown in Figure 1.

The first steps in estimating the cost of the distillation column are to specify the type of column and the construction material and to determine the size. We chose a sieve-tray column made of carbon steel. We began our size estimation by determining the height of the column. We calculated the number of theoretical trays needed by using the McCabe-Thiele method (9). This method uses vapor-liquid equilibrium data, the composition of the feed, the desired distillate and bottoms composition, and the reflux ratio to ascertain graphically the number of theoretical trays. Distillation to 80 wt % ethanol with a reflux ratio of 2.7 requires 14 theoretical trays. By definition, the overall column efficiency equals the ratio of the theoretical number of trays to the actual number of trays. Therefore, the actual number of trays can be computed by taking the quotient of the theoretical number of trays and the efficiency. Although the efficiency varies from plate to plate, the average efficiency for the entire column can be determined from the physical properties (i.e., relative volatility and average viscosity) of the key components (9). For this system, the efficiency approximately equals 72%, and thus the actual number of trays is 20.

To calculate the height of the column, the tray spacing must be known in addition to the number of trays. Tray spacing is selected to minimize entrainment. Trays are normally spaced 12 to 30 in. apart. One reference states that the lower spacings (12 to 15 in.) are used for high-pressure systems and the higher spacings (24 to 30 in.) are used for vacuum systems. Columns operating at or close to atmospheric pressure generally have tray spacings of 18 in. (9). However, another source states that columns with diameters in the range of 4 to 10 ft should have a tray spacing of 24 in. (10). These two sources gave contradicting values for the tray spacing needed for the column we designed. Based on these references, the tray spacing should be either 18 or 24 in. because the operating pressure for the column was only slightly above atmospheric and, as will be shown later, the column diameter fell within the 4- to 10-ft range. We chose the larger spacing, which resulted in a taller, more expensive column, to try to achieve a more accurate cost estimate.

The height was then calculated by multiplying the number of trays by the tray spacing and adding the length of the skirt. The skirt is usually 10 to 15 ft (11). We used 15 ft for our estimate. This resulted in a column with a height of 55 ft.

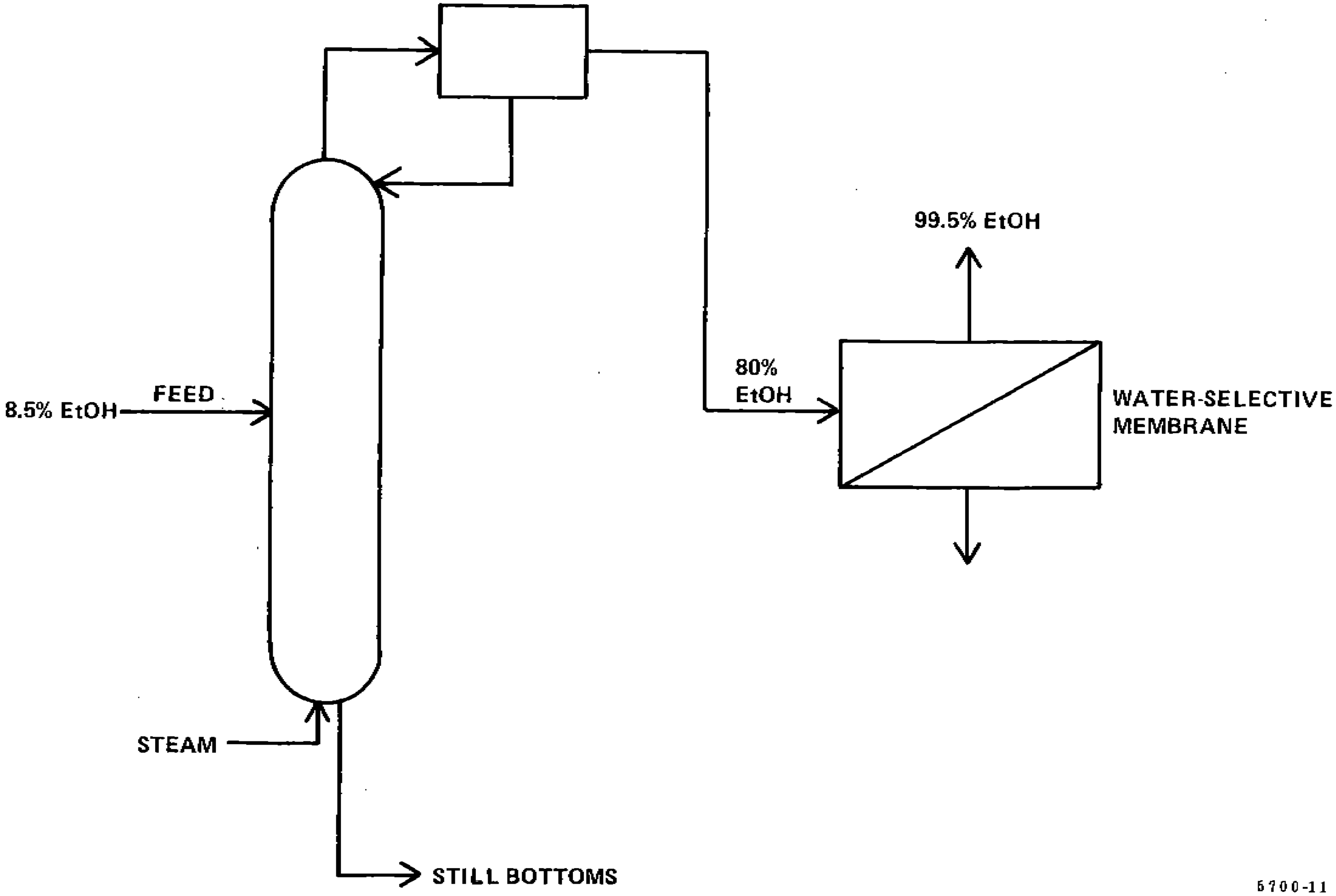
8.5% EtOH
FEED
STEAM
STILL BOTTOMS
80%
EtOH
99.5% EtOH
WATER-SELECTIVE
MEMBRANE
5700-11

Figure 1. Schematic of separation process using distillation combined with water-selective membranes (Case II).

The final step in the size estimation was to determine the column diameter. The column diameter was calculated by the "F-factor" method (9). The "F-factor," F_c, was determined from a plot of F_c as a function of column pressure for tray spacing equal to 24 in. F_c was then used to calculate the area free for vapor flow, via the relation

$$A_f = \frac{W}{F_c \, \rho_v^{1/2}}$$

where W is the vapor mass flow rate (lb/s) and ρ_v is the density of the vapor. The total area was computed by summing the vapor-flow area and the downcomer area, usually assumed to be 5% of vapor-flow area. The diameter of the column was then calculated from the total area.

Finally, the installed cost of the column was calculated. The installed cost included the cost of materials for the shell and trays, cost of tray installation, labor, construction overhead, engineering, and contingencies (11).

The total cost for the distillation part of this process was determined by summing the column cost and costs for the condenser, reboiler, and steam generator. The generator was designed to produce 28,100 kg/h of 250-psig saturated steam. The heat-transfer area required for both the condenser and reboiler was determined by using convection heat-transfer equations. The cost was then estimated using an empirical correlation developed for the ASPEN computer program, which originated at the Massachusetts Institute of Technology (12).

The amount of membrane area required to dehydrate the 80 wt % ethanol distillate was determined using the computer program discussed earlier. We assumed an installed cost of $400/m^2. Figure 2 shows the effect of membrane flux and selectivity on the membrane area required for the dehydration of an 80 wt % feed to a 99.5 wt % product. The data show that the greatest reduction in the required membrane area occurs as the selectivity increases, and the need for recycling the permeate stream can be reduced at higher selectivities. In Figure 3, the area required for dehydration of a specified feed stream to produce a 99.5 wt % ethanol product is presented as a function of selectivity at constant flux. Here again, it is clear that the advantage of increased selectivity diminishes rapidly beyond selectivities of about 50.

In Table 4, we present three cases of this process, each with different membrane characteristics. The diameter of the column was recalculated for each case to reflect the varying amount of the recycle stream returned to the column from the membrane process as the selectivity of the membrane increased. The energy consumption is presented along with the total installed cost for each case.

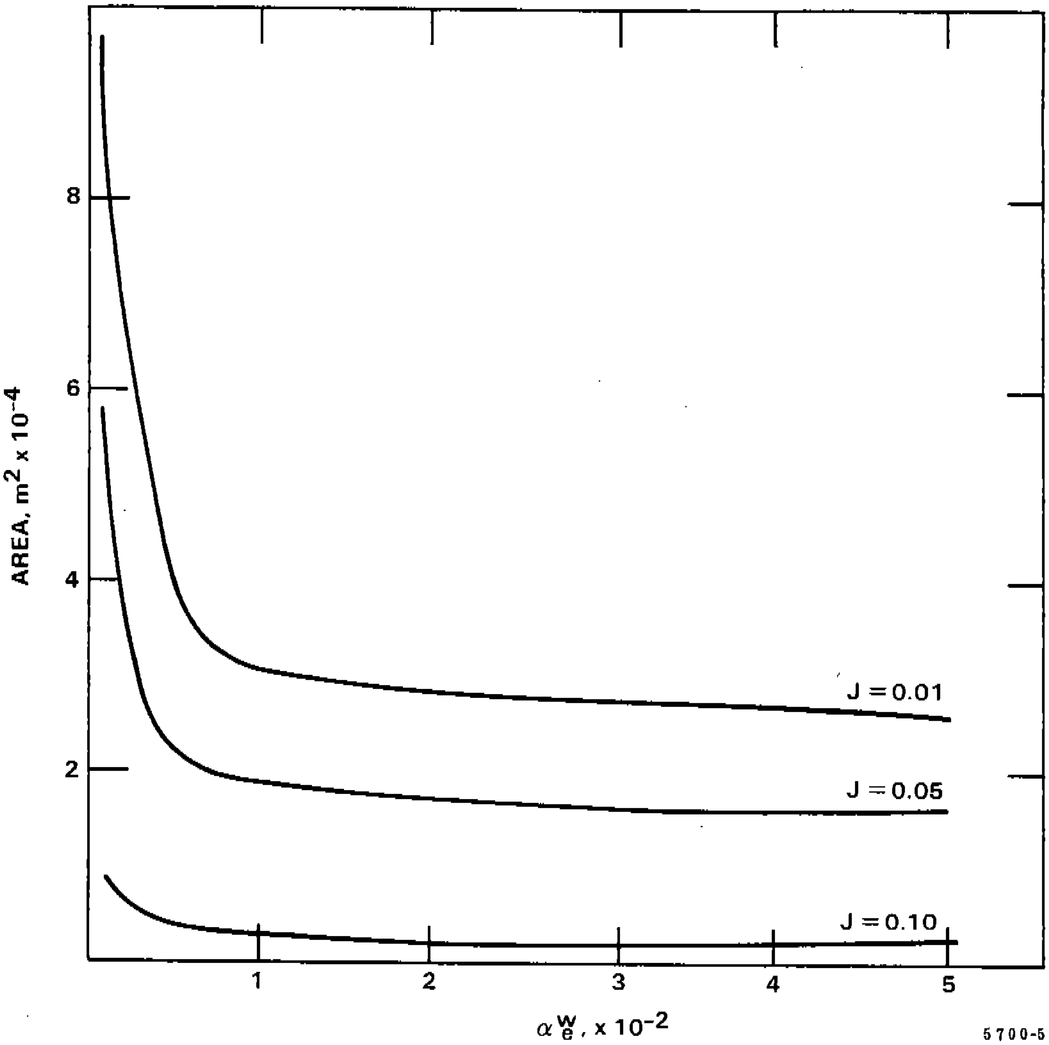

Figure 2. Effect of membrane flux and selectivity on area required to produce 99.5% ethanol from 80% ethanol feed using water-selective membranes.

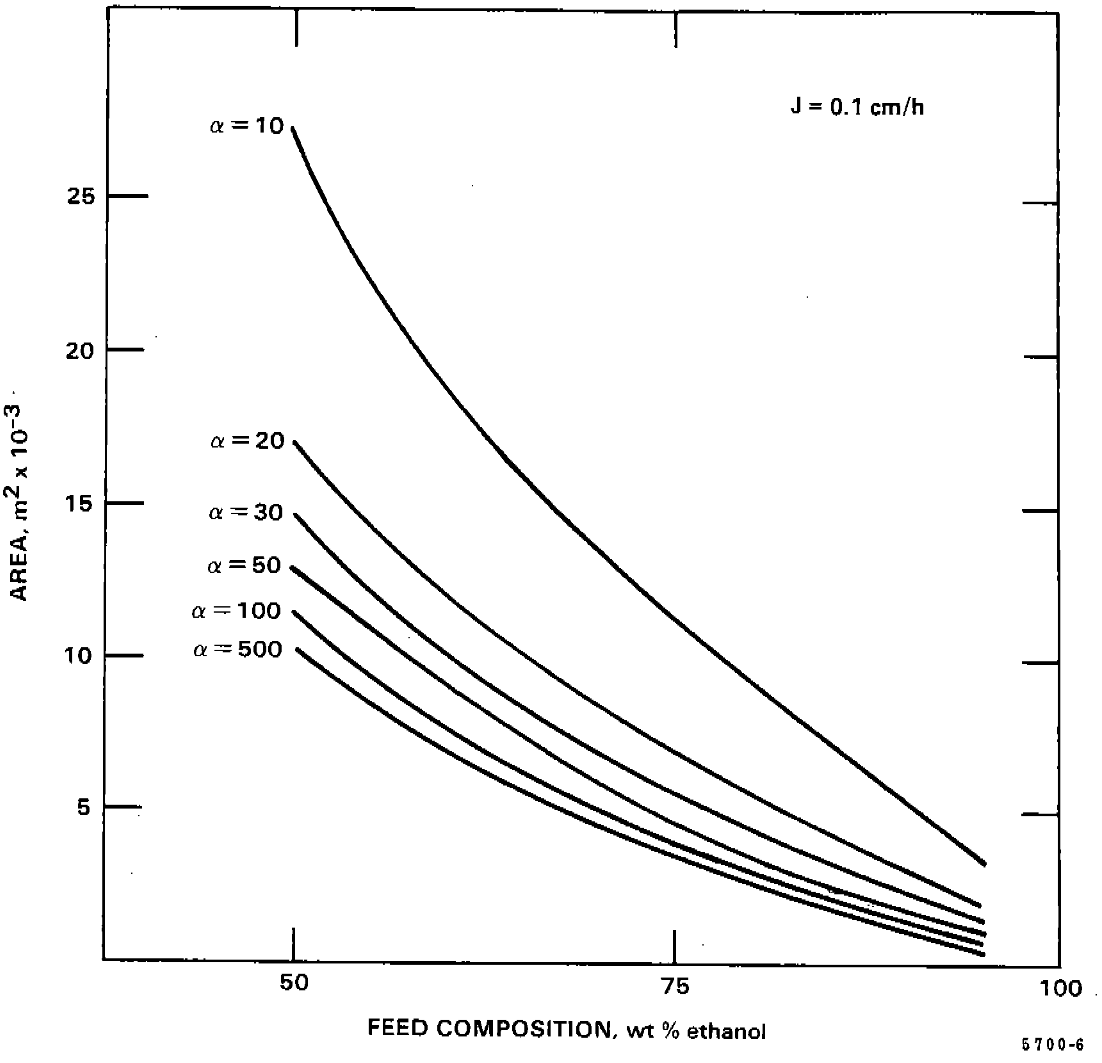

Figure 3. Effect of feed composition and membrane selectivity on area required to produce 99.5% ethanol using water-selective membranes.

TABLE 4. EFFECT OF MEMBRANE CHARACTERISTICS ON CAPITAL COST AND ENERGY REQUIREMENTS--CASE II

α	J, cm/h	Section	Installed cost, \$ x 10^6	Energy requirement, kcal/kg[a]
15	0.13	Distillation[b] (8.8-ft diameter)	1.0	1580
		Pervaporation (3 stages at 1750 m^2)	2.1	170 [280]
			3.1	1750
100	0.10	Distillation[b] (7.8-ft diameter)	0.9	1450
		Pervaporation (3 stages at 1035 m^2)	1.2	80 [180]
			2.1	1530
500	0.10	Distillation[b] (6.8-ft diameter)	0.8	1170
		Pervaporation (3 stages at 900 m^2)	1.1	70 [170]
			1.9	1240

[a] Numbers in brackets represent energy required to vaporize permeate and are excluded from the total energy estimate.
[b] Column is 55 ft tall with 20 trays. Reflux ratio equals 2.7.

2. Case III

This process involves distillation to 40 wt % ethanol and then the use of ethanol-selective membranes to concentrate the permeate to 80 wt % ethanol. Finally, the product is dehydrated to 99.5 wt % by water-selective membranes. A block diagram illustrating this process is shown in Figure 4. The cost estimates for this process were prepared using methods similar to those used for Case II. The column for this process functioned as a stripping column with no reflux returned from the condenser. This required more plates, 19 theoretical and 27 actual, assuming a 72% overall column efficiency. This resulted in a total height of 69 ft including the skirt and a diameter of 6.9 ft.

The total installed cost and the energy requirements for this process are presented in Table 5.

3. Case IV

This process (Figure 5) uses ultrafiltration to remove suspended material from the fermentation beer before ethanol-selective membranes concentrate the beer to 80 wt % ethanol and water-selective membranes dehydrate the stream to yield a 99.5 wt % ethanol product. For both the ethanol- and water-selective membranes, we used our computer program to calculate the membrane area required for various selectivities. Figure 6 shows the membrane areas that are required to reduce the ethanol concentration of an 8.5 wt % feed to 1.0 wt % when ethanol-selective membranes are used. The only ethanol-selective membrane that we found reported in the literature was polydimethylsiloxane. For this material, areas in excess of 1,000,000 m^2 would be required to affect the separation. Clearly, the cost of this process would be prohibitive. When higher selectivities and fluxes are considered, the membrane area decreases but not sufficiently to make the process economical. In Figure 7, the membrane areas required to reduce an 8.5 wt % feed to a specified concentration are presented for a number of selectivities and fluxes. Even when the retentate contains 2.5 wt % ethanol, the required areas are excessive. Accordingly, the use of ethanol-selective membranes in the initial concentration step does not seem economical when compared to a simple beer still. We have summarized the total membrane area, installed cost, and energy requirements for this process in Table 6.

The use of water-selective membranes for the final dehydration step, however, does appear attractive. And, if further improvements in flux and selectivity can be realized, the concentration range over which such membranes can be used can be expanded for essentially no increase in the cost of the membranes. The savings in the cost of distillation equipment should result in an overall reduction in the capital costs for purification. It is clear that the use of ethanol-selective membranes for the removal of ethanol from fermentation beer produced by batch fermentation is not economically feasible given the currently available membranes. Moreover, the improvements in

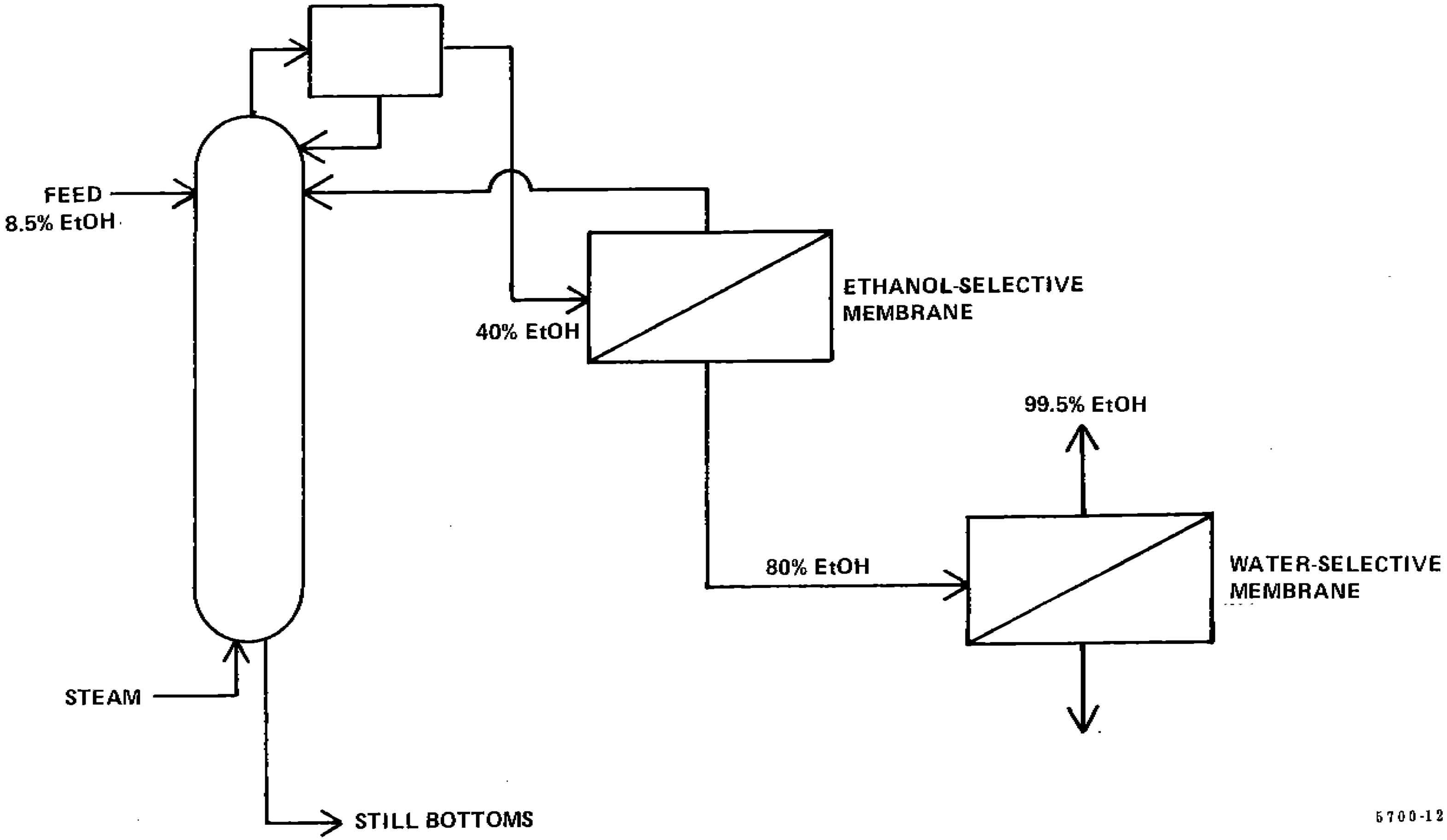
FEED
8.5% EtOH
40% EtOH
ETHANOL-SELECTIVE MEMBRANE
99.5% EtOH
80% EtOH
WATER-SELECTIVE MEMBRANE
STEAM
STILL BOTTOMS
5700-12

Figure 4. Schematic of separation process using distillation combined with both ethanol- and water-selective membranes (Case III).

TABLE 5. CAPITAL COSTS AND ENERGY REQUIREMENTS--CASE III

Section	Installed cost, $\$ \times 10^6$	Energy requirement, kcal/kg[a]
Distillation	0.6	1120
Column: 6.9-ft diameter 69 ft tall 27 trays		
Pervaporation		
Ethanol Selective:	8.6	590 [400]
$\alpha = 16$ $J = 0.10$ cm/h AREA = 21,600 m^2		
Water Selective:	2.1	170 [280]
$\alpha = 15$ $J = 0.13$ cm/h AREA = 5,250 m^2		
	11.3	1880

[a] Numbers in brackets represent energy required to vaporize permeate and are excluded from the total energy estimate.

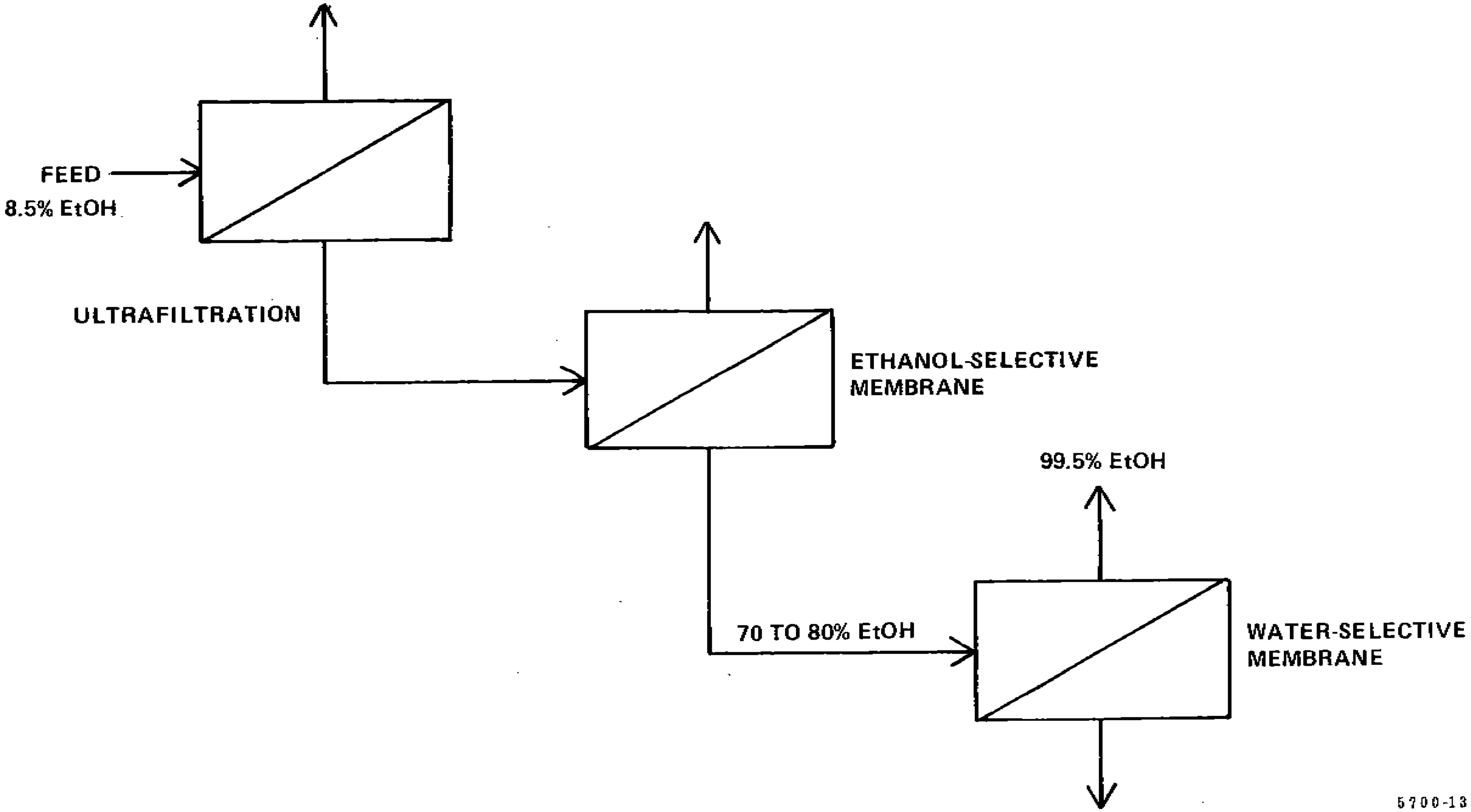
FEED
8.5% EtOH
ULTRAFILTRATION
ETHANOL-SELECTIVE
MEMBRANE
99.5% EtOH
70 TO 80% EtOH
WATER-SELECTIVE
MEMBRANE
5700-13

Figure 5. Schematic of separation process involving ultrafiltration followed by both ethanol- and water-selective membranes (Case IV).

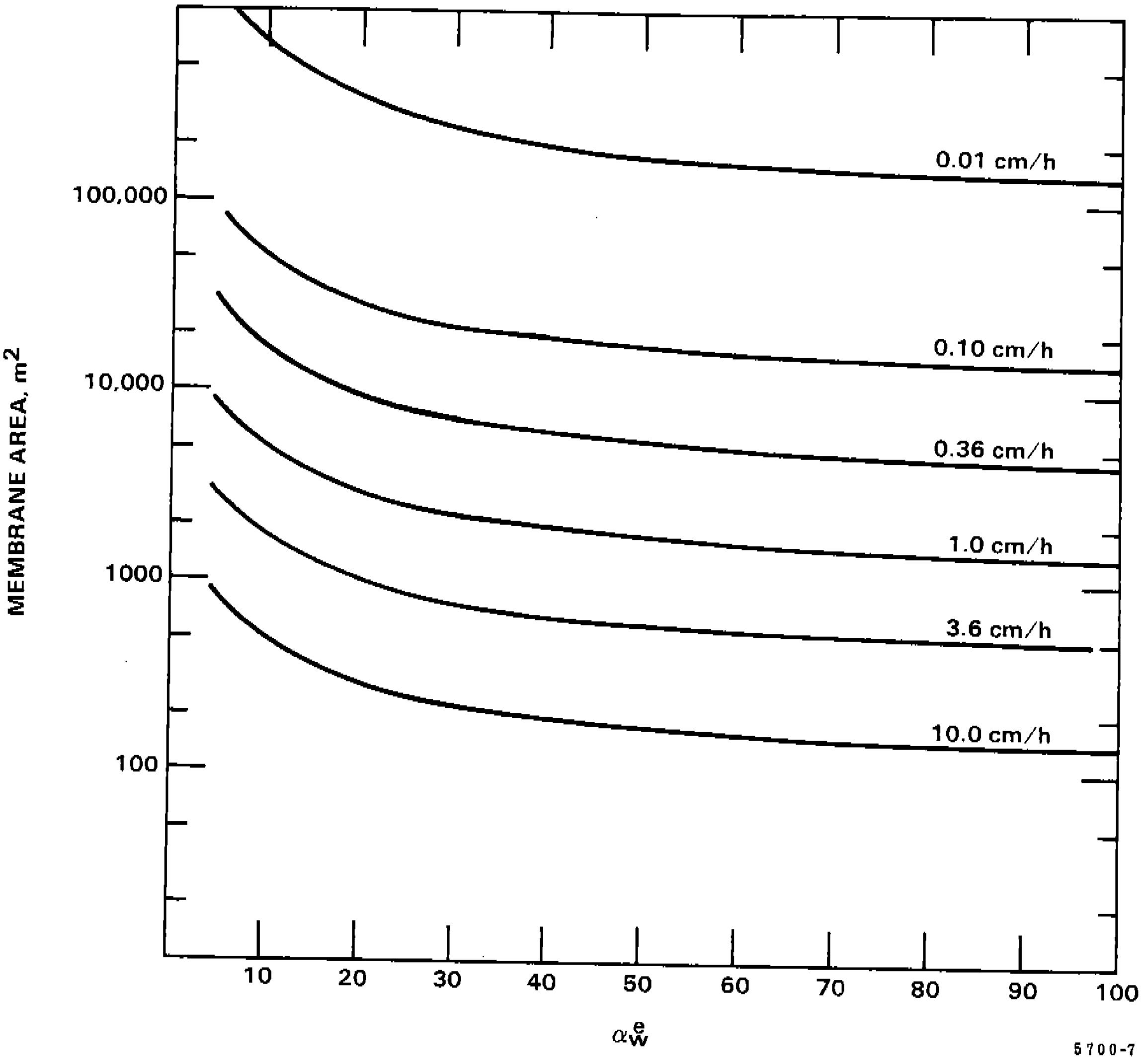

Figure 6. Effect of membrane selectivity and flux on area required to produce a 1.0 wt % ethanol retentate from a 8.5% feed using ethanol-selective membranes.

TABLE 6. EFFECT OF MEMBRANE CHARACTERISTICS ON CAPITAL COST AND ENERGY REQUIREMENTS--CASE IV

Ethanol selective				Water selective				Total		
α	Concentration, wt %	Area, m^2	Energy[a], kcal/kg	α	Concentration, wt %	Area, m^2	Energy, kcal/kg	Area, m^2	Installed cost, $ x 10^6	Energy, kcal/kg
19	8.5-80	69,400	2790 [1190]							3980
				50	80-99.5	3700	200 [230]			430
								73,100	29.2	4410
50	8.5-54	26,600	1330 [680]							2010
				50	54-99.5	10900	600 [450]			1050
								37,500	15.0	3060
100	8.5-70	20,300	1050 [570]							1620
				50	70-99.5	5800	330 [300]			660
								26,100	10.4	2280
100	8.5-70	19,500	1000 [560]							1560
				100	70-99.5	5000	290 [280]			570
								24,500	9.8	2130

(continued)

TABLE 6 (continued)

Ethanol selective				Water selective				Total		
α	Concentration, wt %	Area, m^2	Energy,[a] kcal/kg	α	Concentration, wt %	Area, m^2	Energy, kcal/kg	Area, m^2	Installed cost $\$ \times 10^6$	Energy, kcal/kg
100	8.5-70	18,800	970 (540)							1510
				500	70-99.5	4500	270 (260)			530
								23,300	9.3	2040 (800)
500	8.5-92	15,000	810 (480)							1290
				50	92-99.5	1500	80 (140)			220
								16,500	6.6	1510 (620)

[a] Numbers in brackets represent energy for vaporization of permeant and are included in the total energy requirement.

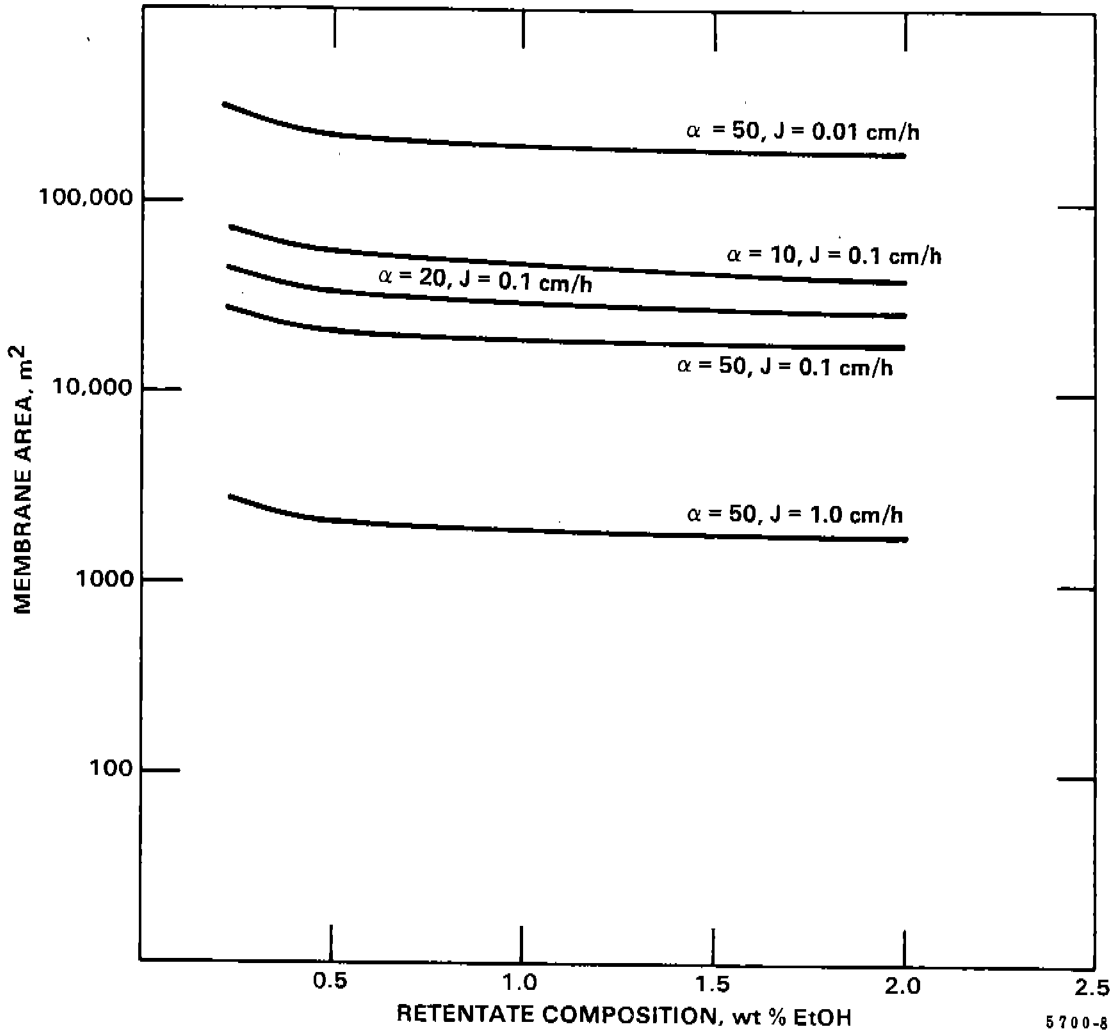

Figure 7. Area required to achieve specified retentate composition from 8.5 wt % ethanol feed using ethanol-selective membranes.

membrane performance that will be required to make this process economical are substantial. The reason for this is the low ethanol content in the retentate that is needed to avoid significant product loss. On the other hand, in a continuous fermentation, ethanol-selective membranes could be used for continuous product recovery to maintain the ethanol concentration below the level where significant inhibition of the fermentation rate occurs. At higher feed concentrations (for example, 40 wt %), ethanol-selective membranes may be useful for preparing a higher concentration feed for the water-selective membranes. Accordingly, the process described in Case III may become advantageous as better membranes are developed.

D. Waste-Treatment Section

Whether an 8.5% beer is purified by a distillation process, by some combination of beer still and membrane process, or by membrane processes alone, the wastes produced must be treated to meet the Environmental Protection Agency's requirements. In December 1983, we estimated the cost of facilities to treat the wastes (stillage) from a 28,125,000-L/yr ethanol plant. We adjusted these turnkey costs from 28,125,000 L/yr to 95,000,000 L/yr by the Chemical Engineering 0.6 factor (i.e., $[(95,000,000)/(28,125,000)]^{0.6}$ x cost of 28,125,000-L/yr facilities. We then updated the cost from December 1983 to 1985.

The major items of equipment in the waste-treatment section are a flash tank complete with blower to reduce the temperature of the stillage from 105 to 50 °F, a heat exchanger to reduce the temperature to 36 °C, a packaged anaerobic digestor to reduce the biological oxygen demand (BOD) by 85%, and an anaerobic lagoon to complete the reduction of BOD to meet EPA requirements.

The 1983 cost of the waste-treatment section for the 28,125,000-L/yr plant was $1,985,000. The cost of a facility for a 95,000,000-L/yr plant was $4,090,000 (by the 0.6 factor). The cost updated to 1985 by the MS indices is $4,195,900.

IV. MEMBRANE DEVELOPMENT

A. Introduction

One of the two major efforts of this project was directed toward the design, fabrication, and evaluation of membranes for use in pervaporation units. Initially, the scope of this project involved the preparation and evaluation of ethanol-selective membranes only. However, when we concluded our economic evaluations, we determined that ethanol-selective membranes were not a feasible replacement for distillation in alcohol-water separations in terms of capital costs. Our economic estimates did indicate that water-selective membranes held a greater potential for reducing the costs of ethanol purification. Therefore, it was decided at the contractor's review meeting held June 10 through 12, 1985, in Denver, Colorado, that we would develop and test water-selective membranes during the remainder of the project. The overall goal of the laboratory phase of this project was to determine throughput rates and selectivity values for experimental membranes. In the following sections we will present an explanation of our experimental procedure and the results obtained.

B. Procedure for Evaluating Membranes

The experimental pervaporation apparatus consisted of a thin-channel, laminar-flow, spiral-path cell. A Masterflex tubing pump was used to deliver feed at the rate of 25 cm^3/min to the cell. The feed supply and the test cell were maintained in a 45 °C water bath. The membrane was supported on one side by a porous disk, which also served to evenly distribute the vacuum, while the feed was circulated on the other surface. The surface area of the membrane through which mass transfer took place was 139 cm^2. Cold-finger traps cooled by dry ice/isopropyl alcohol were used to collect the permeate. We made no attempts to evaluate the downstream pressure as an independent variable in our evaluations. However, we did operate the vacuum pump at full power to deliver the lowest possible pressure.

The composition of the permeate was determined by measuring the refractive index of the permeate mixture and then calculating the concentration from a calibration curve of refractive index vs concentration. We determined the throughput rate from the amount of material captured in the traps and the selectivity by using the expression:

$$\alpha_w^e = \frac{\left(\frac{Y_e}{Y_w}\right)_p}{\left(\frac{X_e}{X_w}\right)_f} \tag{14}$$

where p and f denote the permeate and feed, respectively, y denotes the weight fractions of the components in the vapor phase, and x denotes weight fractions in the liquid phase.

After placing a new membrane in the test cell, the system was allowed to operate (feed was circulating and vacuum was applied) for a minimum of 30 min before the initiation of the first sample collection.

C. Ethanol-Selective Membranes

During the initial phase of this project we conducted an intensive literature review for information on pervaporation and the use of membranes in ethanol purification. Data obtained from the survey was summarized previously in Table 1 of this report. The only material identified by the survey that showed ethanol selectivity was the rubbery polymer polydimethylsiloxane (PDMS). In previous work done here with ethanol-selective membranes, we demonstrated that incorporating materials with strong attractive forces for water molecules but not for ethanol molecules into a polymeric matrix resulted in ethanol selectivity. A PDMS membrane containing 3A molecular sieves exhibited the best separation factor of all the membranes evaluated during the previous study although the corresponding throughput rate for this membrane was only a fraction of the rate achieved by an unfilled membrane. Based on this, we suspected that greater sieve loading would enhance ethanol selectivity at the expense of throughput rates. Therefore, for our laboratory studies we chose to prepare membranes from PDMS alone and to prepare membranes using two different sieve-loaded concentrations to determine the effect of sieve loading on throughput rate and separation factor.

Three types of composite membranes were prepared: PDMS (MDX4-4210, medical grade, Dow Corning, Midland, MI), 10% sieve-loaded PDMS (3A molecular sieves, Aldrich Chemical Company, Milwaukee, WI), and 20% sieve-loaded PDMS. The membranes were hand-cast onto a glass plate under ambient conditions. Membranes were then cured in an 80 to 85 °C oven overnight. The average thickness of each was 7.5, 8.75, and 10 mils respectively.

We evaluated the ethanol-selective membranes at various feed concentrations ranging from 7.8 to 40.5 wt % ethanol. In Table 7, we summarize the results obtained by presenting the mean and standard deviation for flux, selectivity, and permeate composition for each of the membranes evaluated. The

TABLE 7. SUMMARY OF RESULTS FROM EVALUATION OF POLYDIMETHYLSILOXANE

Membrane[a]	Date of evaluation, 1985	Concentration, wt % ETOH Feed	 Permeate	Flux, g/h	α_W^E
C968-33	4/5	10.0	36.3 ± 6.5	0.83 ± 0.77	5.28 ± 1.46
C968-33	4/8-4/10	10.0	55.5 ± 22.2	0.84 ± 0.56	18.16 ± 17.79
C968-33	4/6	10.0	40.3 ± 2.9	0.75 ± 0.12	6.15 ± 0.70
C968-33	5/2	10.0	42.4 ± 2.4	0.76 ± 0.12	6.15 ± 0.70
C968-33	5/9-5/10[b]	10.0	28.5 ± 17.4	0.56 ± 0.19	4.25 ± 2.92
C968-33	5/10[c]	10.0	42.2 ± 0.9	0.61 ± 0.07	6.63 ± 0.26
C968-33	5/13	7.8	36.5 ± 4.9	0.67 ± 0.05	7.83 ± 0.43
C968-33	5/14	19.6	66.0 ± 3.8	1.08 ± 0.08	8.10 ± 1.52
C968-33	4/11-4/12	40.0	79.3 ± 1.9	2.10 ± 0.39	5.74 ± 0.70
C968-33	5/16	39.6	78.4 ± 1.2	1.31 ± 0.13	5.55 ± 0.38
C968-33	5/17	39.6	75.3 ± 2.6	1.49 ± 0.40	4.68 ± 0.60
C968-33	5/24	40.5	74.4 ± 3.8	1.24 ± 0.38	4.34 ± 0.77
C968-33	5/28	37.0	74.7 ± 2.1	1.47 ± 0.17	5.07 ± 0.56
C968-34	5/2	10.0	40.0 ± 4.3	0.68 ± 0.25	6.12 ± 1.00
C968-34	5/9-5/10	10.0	41.7 ± 6.6	0.54 ± 0.28	6.64 ± 1.53
C968-34	5/13	7.83	42.7 ± 0.6	0.47 ± 0.04	8.78 ± 0.21
C968-34	5/14	19.62	68.5 ± 3.6	0.75 ± 0.06	9.02 ± 1.35
C968-34	5/16	39.6	77.5 ± 2.9	0.88 ± 0.19	5.35 ± 0.96
C968-34	5/17	39.6	77.2 ± 1.3	1.00 ± 0.09	5.17 ± 0.41
C968-34	5/24	40.5	79.7 ± 1.8	1.13 ± 0.05	5.83 ± 0.69
C968-34	5/28	37.0	78.3 ± 6.0	1.23 ± 0.11	6.58 ± 2.16
C968-35	5/9-5/10	10.0	37.8 ± 9.5	0.53 ± 0.5	5.77 ± 1.91
C968-35	5/13	7.83	35.7 ± 6.9	0.33 ± 0.05	6.69 ± 1.86
C968-35	5/14	19.62	69.7 ± 4.0	0.53 ± 0.03	9.63 ± 1.92
C968-35	5/16	39.6	75.9 ± 8.8	0.59 ± 0.19	5.34 ± 1.82
C968-35	5/17	39.6	74.2 ± 2.7	0.81 ± 0.05	4.43 ± 0.57
C968-35	5/24	40.5	79.6 ± 2.2	0.77 ± 0.06	5.81 ± 0.8
C968-35	5/28	37.0	72.2 ± 8.0	0.92 ± 0.14	4.79 ± 1.75

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[a] C968-33 is homogeneous membrane; C968-34 is 10% sieve loaded; C968-35 is 20% sieve loaded.

[b] Includes only data collected on 5/10 of the two-day evaluation.

[c] System ran continuously, but no sample was collected for analysis during the night.

deviation tended to be large because the data exhibited an oscillating trend. Both the flux and permeate composition values exhibited this trend but were mirror images of each other. The average flux and permeate composition for each membrane expressed as a function of feed composition are presented in Figures 8 and 9. As shown by the figures, there is a decrease in flux accompanied by a slight increase in permeate concentration as the sieve loading increased. We found that a sieve loading of 10% yielded an improvement of 17.5% in selectivity at 20 wt % ethanol feed concentration. However, when the sieve loading was increased to 20%, no further improvements in selectivity were observed. Also, when the feed concentration was increased to 40 wt % ethanol, the improvements resulting from to a 10% sieve loading decreased to 14.5%. Our experimental results showed the greatest separation occurred using 10% sieve-loaded membranes at a 20 wt % ethanol feed concentration. It should be noted that, while there was only a negligible difference in the selectivity exhibited by the 20% sieve-loaded compared to the 10% sieve-loaded membrane, there was a noticeable decrease in flux as the sieve loading increased. It follows that sieve loading in excess of 10% tended to defeat the purpose of preparing a highly ethanol-selective membrane while maintaining a high flux across the membrane.

D. Water-Selective Membranes

Our strategy for the development of water-selective membranes was based on the concept of creating a water-enriched boundary layer at the upstream surface of the membrane. To achieve this, we envisioned a composite membrane consisting of an asymmetric, microporous support and a thin surface layer of a hydrophilic material. By using a microporous support, we felt that we would be able to prepare membranes with extremely thin active layers that would have acceptable physical properties. For the active surfaces, we believed that polar moieties such as hydroxyl of carboxyl groups on the upstream surface of the membrane would tend to attract water to a greater extent than ethanol creating a water-rich boundary layer. The ultimate effect should be to improve the water selectivity of the membrane.

Obviously, such groups would need to be tightly bound to the surface of the support membrane to prevent their removal by the flowing feed stream. To do this, we felt that grafting by a wet chemical technique was preferred. We chose to use acrylic monomers and to graft onto cellulosic substrates using ceric ion as the initiator.

1. Membrane Fabrication

Based on our initial literature search, we concluded that cellulose acetate showed the most promise for preparing water-selective membranes for the dehydration of ethanol from 80 to 99.5 wt %. Therefore, we focused our laboratory evaluations on membranes cast from this polymer.

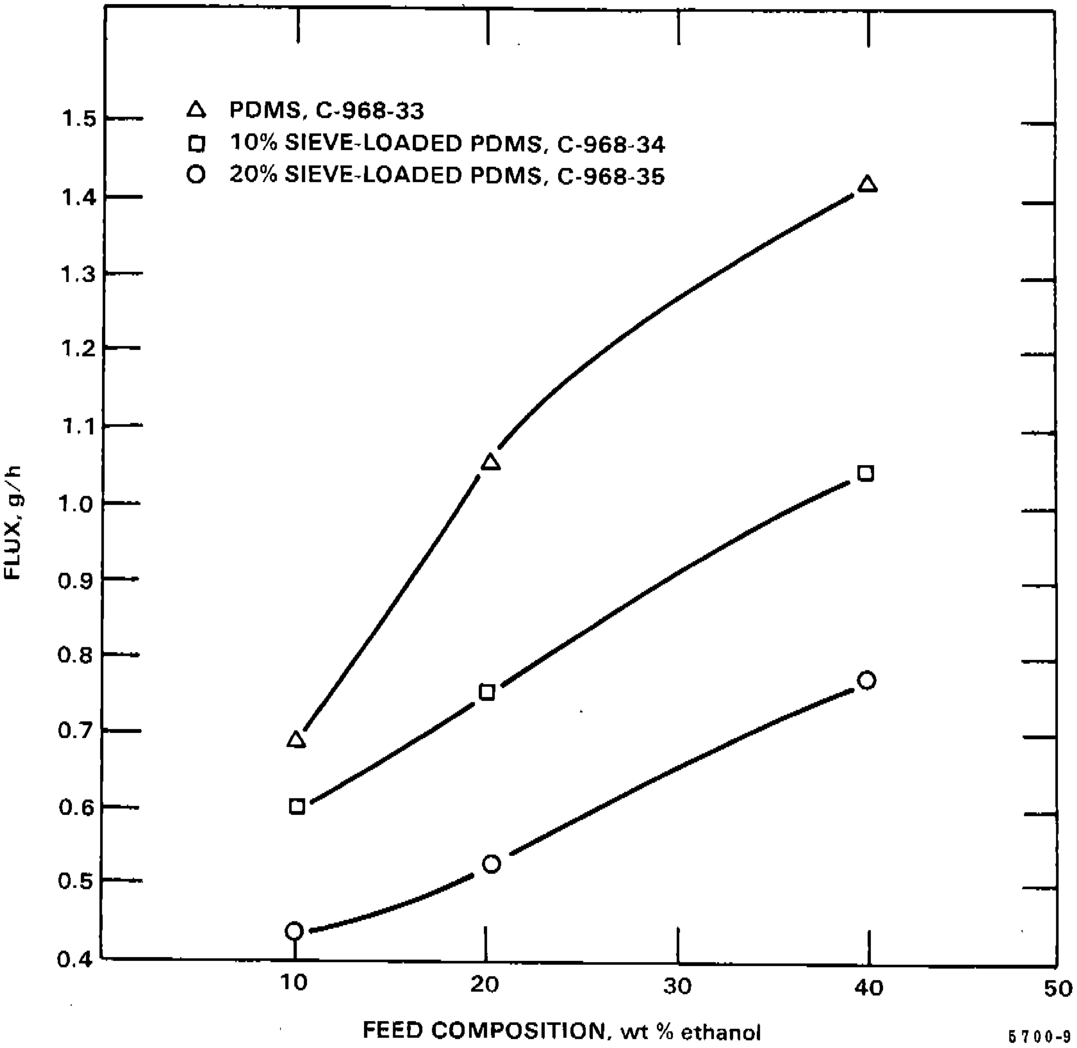

Figure 8. Flux as a function of feed composition for PDMS membranes.

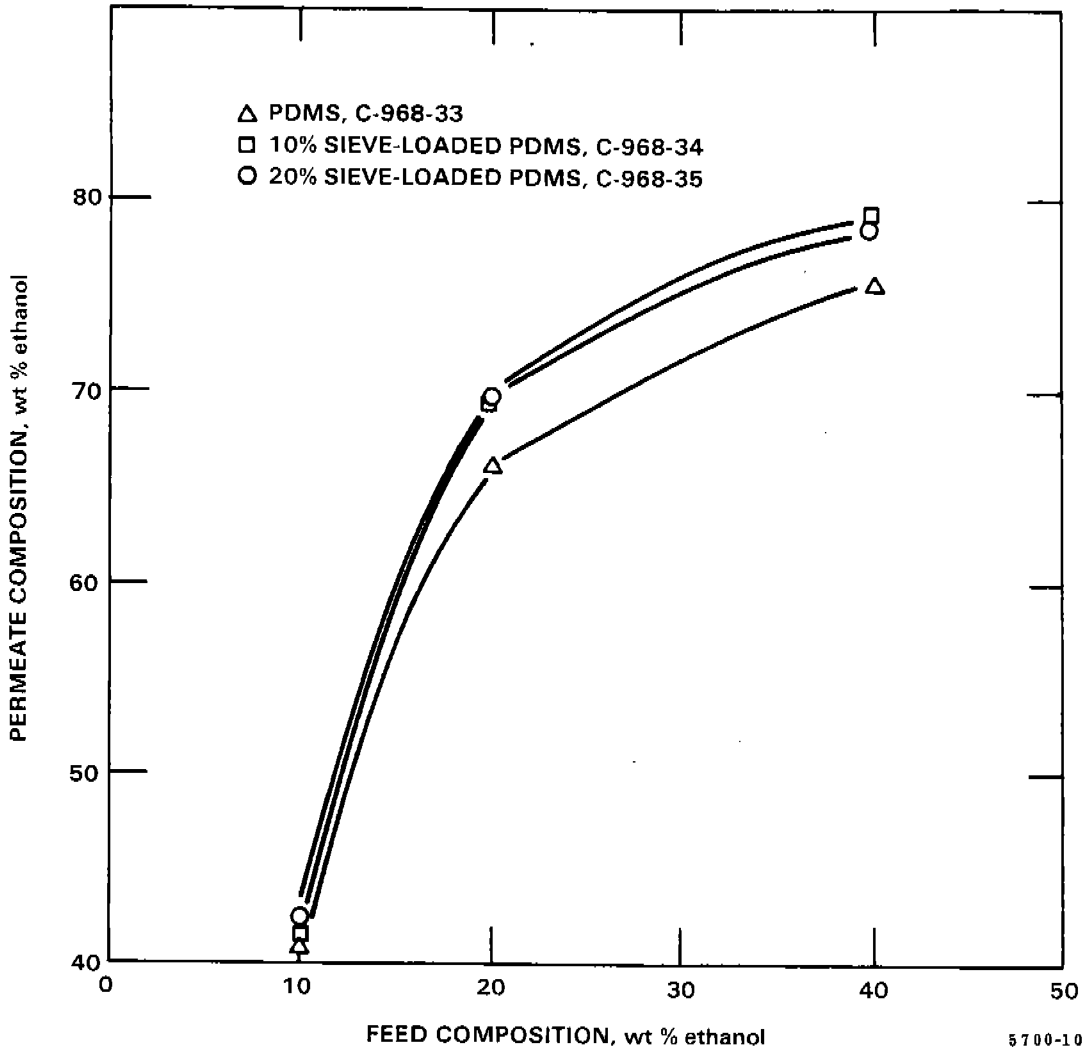

Figure 9. Permeate compositive as a function of feed composition for PDMS membranes.

To begin our laboratory evaluations, we prepared homogeneous cellulose acetate membranes ranging in thickness from 0.5 to 6.0 mils, with the majority averaging 2 mils. As we began our laboratory studies on water-selective membranes, our ultimate goal was to prepare asymmetric membranes that had a thin, dense skin supported by a finger like structure. This type of asymmetric structure was thought to offer the best selectivity at the highest possible flux. By preparing and evaluating homogeneous membranes first, we could determine the degree of selectivity exhibited by cellulose acetate membranes while using thicker, denser membranes that were less prone to rupture during preparation and evaluation. However, time did not permit us to prepare and test asymmetric membranes as we had hoped, although we did prepare and evaluate a number of homogeneous cellulose acetate membranes.

All homogeneous membranes were cast on a glass plate using a 10-in. Bradley blade and allowed to air-dry at ambient conditions. Liquinox soap was used as the releasing agent. We tried casting solutions ranging from 4 to 20 wt % polymer but found solutions containing approximately 17.5 wt % yielded the best membranes. We also altered the casting thickness to achieve membranes with no obvious surface imperfections. We found that membranes cast at 35 mils wet thickness from a 17.5 wt % polymer solution in acetone would result in a dry membrane 2 to 3 mils thick. Casting solvents other than acetone were tried, but membranes cast from acetone proved to be the best.

We attempted to improve the water-selectivity of homogeneous cellulose acetate membranes by modifying one surface of the membrane to make it more hydrophilic. Our reasoning was that a hydrophilic surface should attract water molecules from the ethanol and water mixture and thus enhance selectivity. We attempted to modify these cellulosic membranes by grafting monomers onto the surface using ceric ion initiation. A large number of papers discuss using Ce(IV) as the initiator for graft copolymerization of monomers onto cellulosic materials. For example, Mishra in discussing 14 different methods of graft copolymerization points out that the system initiated by ceric ion has a high grafting efficiency compared to other redox systems (13). The greater efficiency results from the formation on the cellulose of free radicals capable of initiating vinyl polymerization when cellulose is oxidized by ceric salts. The radicals are produced almost exclusively on the cellulose; therefore, grafting is favored more than homopolymer formation. However, the exact mechanism of interaction between ceric ion and cellulose has not been confirmed.

In the laboratory, we prepared and evaluated several cellulose acetate membranes on which we attempted surface grafting. The grafting procedure involved the following steps. First, the membrane was placed in the grafting cell. The grafting was performed in a 6-in.-diameter recessed cell with a plexiglass top sealed by an O-ring. The lid contained two injection ports for the grafting solution. Before treatment with the solutions, the cell was thoroughly flushed with nitrogen. The two solutions were 0.1 M ammonium cerium nitrate in 1 M nitric acid and 0.08 M hydroxyethyl methacrylate (HEMA) in deionized (DI) water. Both solutions were prepared, purged with nitrogen, and sealed in serum vials. Initially, the next step of the procedure was to prepare either a 4, 8, or 16 mM solution of ceric ion in the HEMA solution, bubble nitrogen through the solution, and then inject it into the grafting cell. The reaction was allowed to take place for 2 h. At that time, the solution was drawn from the cell, and DI water was injected. The injection and withdrawal of the DI water was repeated several times. The membrane was then removed from the cell and air-dried overnight. Weight gain of the membrane during grafting was used to confirm the presence of a graft.

In an attempt to enhance grafting, we included another step in our procedure. We prepared solutions of 4, 8, or 16 mM concentrations of ceric ion in nitric acid, purged these with nitrogen, and sealed them in serum vials. The solution corresponding to the appropriate concentration of ceric ion in HEMA solution to be used for the grafting was injected into the cell after flushing with nitrogen. This solution remained for 2 h. It was then removed, and the ceric ion/HEMA solution was injected. The remainder of the procedure was the same as described previously. We found no evidence that this enhanced grafting. Weight gains using the initial procedure were comparable to weight gains using the revised procedure.

2. Results

The results obtained from the evaluation of homogeneous membranes of cellulose acetate and from membranes grafted with HEMA using both 4 and 8 mM initiator concentration are summarized in Tables 8 and 9. Although we tried to surface graft using 16 mM concentration, we did not achieve a graft as evidenced by the lack of weight gain during the procedure. In these tables we present the mean and the standard deviation for each evaluation. The deviations tended to be large in many cases. The reason for this is that the data tended to exhibit an oscillating behavior in the same manner as the PDMS membranes previously discussed. Both the permeate composition and the flux values exhibited this trend. However, the curves tended to be mirror images of each other. For example, the data collected during a one-day evaluation of one of the cellulose acetate membranes are shown in Figure 10.

Two cellulose acetate membranes were evaluated at feed concentrations ranging from 83 to 95 wt % ethanol. These membranes yielded selectivities of approximately 19 at 83% feed and 5 at 95%. The average selectivity, flux, and permeate composition for the two membranes as a function of feed composition is shown in Figure 11. This is the expected trend because as the concentration of the feed increases, the separation becomes more difficult. Some membranes reach a point where the selectivity equals one. At this point, the condition of permeatropism exists. .Permeatropism for membrane separations is analogous to an azeotrope in distillation. The concentration at which permeatropism exists can be altered by a change in operating temperature, whereas an azeotrope in distillation can be altered by a pressure change. Because we did

TABLE 8. SUMMARY OF RESULTS FROM EVALUATIONS OF CELLULOSE ACETATE MEMBRANES (NONGRAFTED)

Membrane	Thickness, mils	Concentration, wt % ETOH		Flux, g/h	α_W^E
		Feed	Permeate		
C968-65-5	≈6.0	79.5	27.0 ± 9.3	3.28 ± 0.27	12.27 ± 7.06
C968-68-1	≈0.5	79.5	32.7 ± 5.4	5.11 ± 0.85	8.18 ± 1.85
C968-79-B	≈0.5	76.4	51.2 ± 16.3	4.76 ± 4.23	3.63 ± 2.26
C968-84-A[a]	2.0	76.4	10.9 ± 2.1	2.21 ± 0.90	64.98 ± 12.25
C968-84-G	2.0	77.2	14.1 ± 3.4	3.15 ± 0.98	14.08 ± 3.36
C968-89E	4.0	83.4	21.9 ± 5.7	3.37 ± 0.88	19.62 ± 8.50
C968-89E	4.0	85.6	38.2 ± 0.5	3.80 ± 0.68	9.65 ± 0.22
C968-89E	4.0	87.5	41.8 ± 4.4	3.32 ± 0.29	9.86 ± 1.84
C968-89E	4.0	95.0	80.0 ± 9.1	2.72 ± 0.66	5.05 ± 2.64
C968-89F	4.0	83.4	22.7 ± 6.4	2.46 ± 0.73	18.97 ± 8.66
C968-89F	4.0	85.6	39.1 ± 0.1	3.09 ± 0.31	9.28 ± 0.04
C968-89F	4.0	87.5	42.1 ± 4.3	3.02 ± 0.56	9.73 ± 1.76
C968-89F	4.0	95.0	82.1 ± 9.1	1.93 ± 0.29	4.42 ± 2.54

[a] Extreme swings in flux and permeate composition were recorded throughout the evaluation of this membrane.

TABLE 9. SUMMARY OF RESULTS FROM EVALUATIONS OF GRAFTED CELLULOSE ACETATE MEMBRANES

		Grafting data				Pervaporation data			
				Weight gain		Concn, wt % ETOH			
Membrane	Thickness, mils	Initiator concn, mM	Monomer concn, mM	g	%	Feed	Permeate	Flux	α_E^W
C968-80	≈0.5	4	76.8	a	a	76.4	30.6 ± 7.0	5.61 ± 2.30	7.92 ± 3.13
C968-85	2.0	4	76.8	0.045	3.8	83.5	1.3 ± 1.8	21.36 ± 11.32	1258 ± 1064
C968-85	2.0	4	76.8	0.045	3.8	77.2	29.8 ± 7.0	3.80 ± 0.88	8.40 ± 2.68
C968-86	2.0	4	76.8	0.038	3.8	77.2	24.3 ± 6.4	6.00 ± 2.65	11.31 ± 3.25
C968-87B	2.0	4	76.8	a	a	77.2	22.4 ± 3.8	2.82 ± 0.56	12.51 ± 3.20
C968-89A	3.0	4	76.8	a	a	78.8	26.8 ± 25.9	8.52 ± 10.82	27.39 ± 26.96
C968-93-1	2.0	4	76.8	0.048	3.8	80.0	30.4 ± 10.7	3.09 ± 0.6	10.89 ± 7.55
C968-93-1	2.0	4	76.8	0.048	3.8	82.0	77.2 ± 4.4	20.91 ± 5.98	1.36 ± 0.35
C968-93-2	2.0	4	76.8	0.038	3.6	80.0	31.6 ± 5.5	2.27 ± 0.50	9.14 ± 2.42
C968-93-2	2.0	4	76.8	0.038	3.6	82.0	51.0 ± 22.2	11.39 ± 12.90	5.86 ± 4.77
C968-87A	2.0	8	73.6	0.050	3.1	77.2	9.3 ± 5.1	7.29 ± 3.02	51.71 ± 50.82
C968-92-2	2.0	8	73.6	a	a	83.0	35.8 ± 6.8	2.96 ± 0.66	9.29 ± 3.21
C968-92-2	2.0	8	73.6	a	a	84.7	29.9 ± 1.7	3.30 ± 0.15	13.05 ± 1.03
C968-92-2	2.0	8	73.6	a	a	92.2	42.1 ± 1.0	2.20 ± 0.05	16.26 ± 0.69
C968-92-1	4.0	8	73.6	0.043	4.1	77.7	31.8 ± 2.1	4.46 ± 0.40	7.53 ± 0.73
C968-92-1	4.0	8	73.6	0.043	4.1	83.0	64.5 ± 8.3	9.48 ± 3.89	2.77 ± 0.96
C968-92-1	4.0	8	73.6	0.043	4.1	78.9	28.2 ± 8.8	5.93 ± 1.22	10.88 ± 5.85

[a] Not taken.

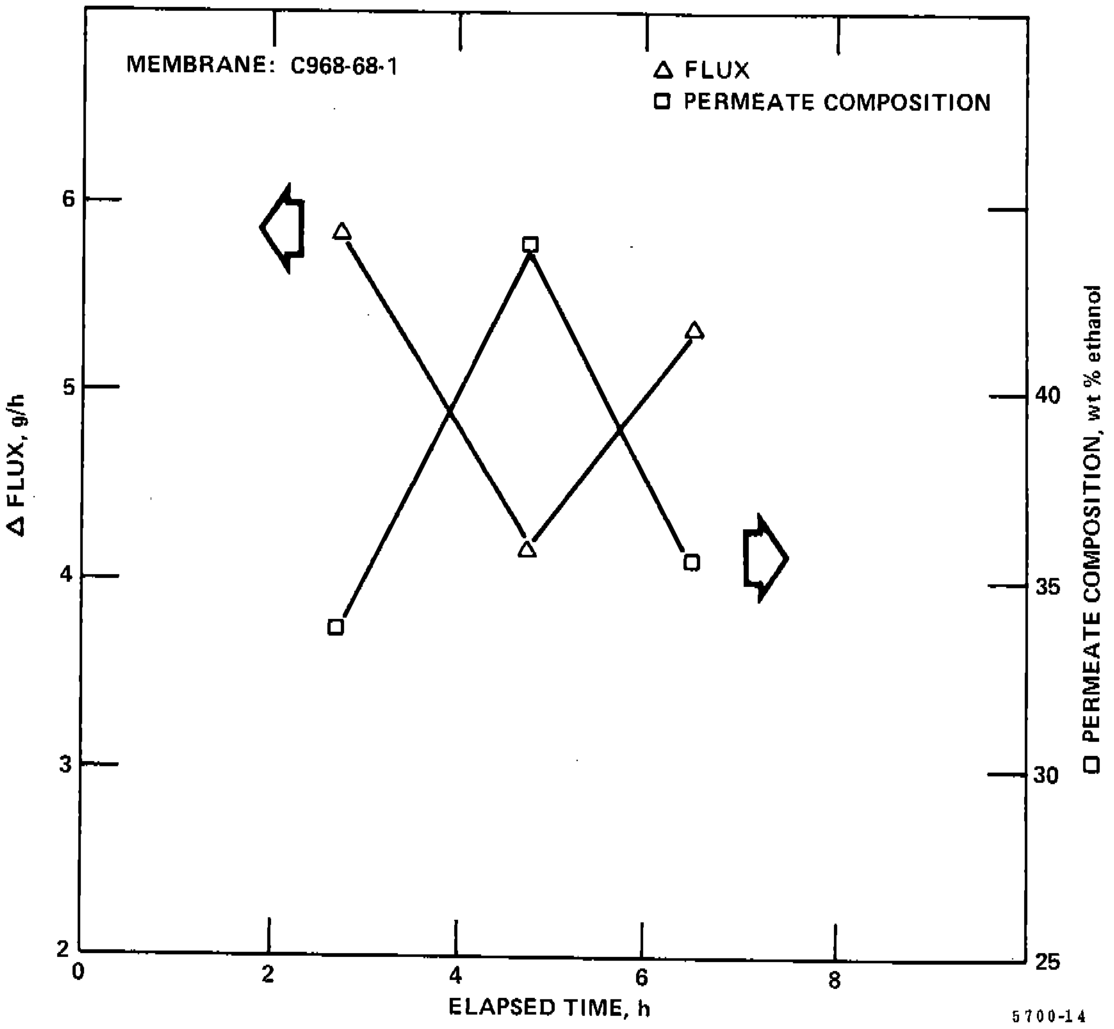

Figure 10. Plot of data from one day's evaluation of a cellulose acetate membrane.

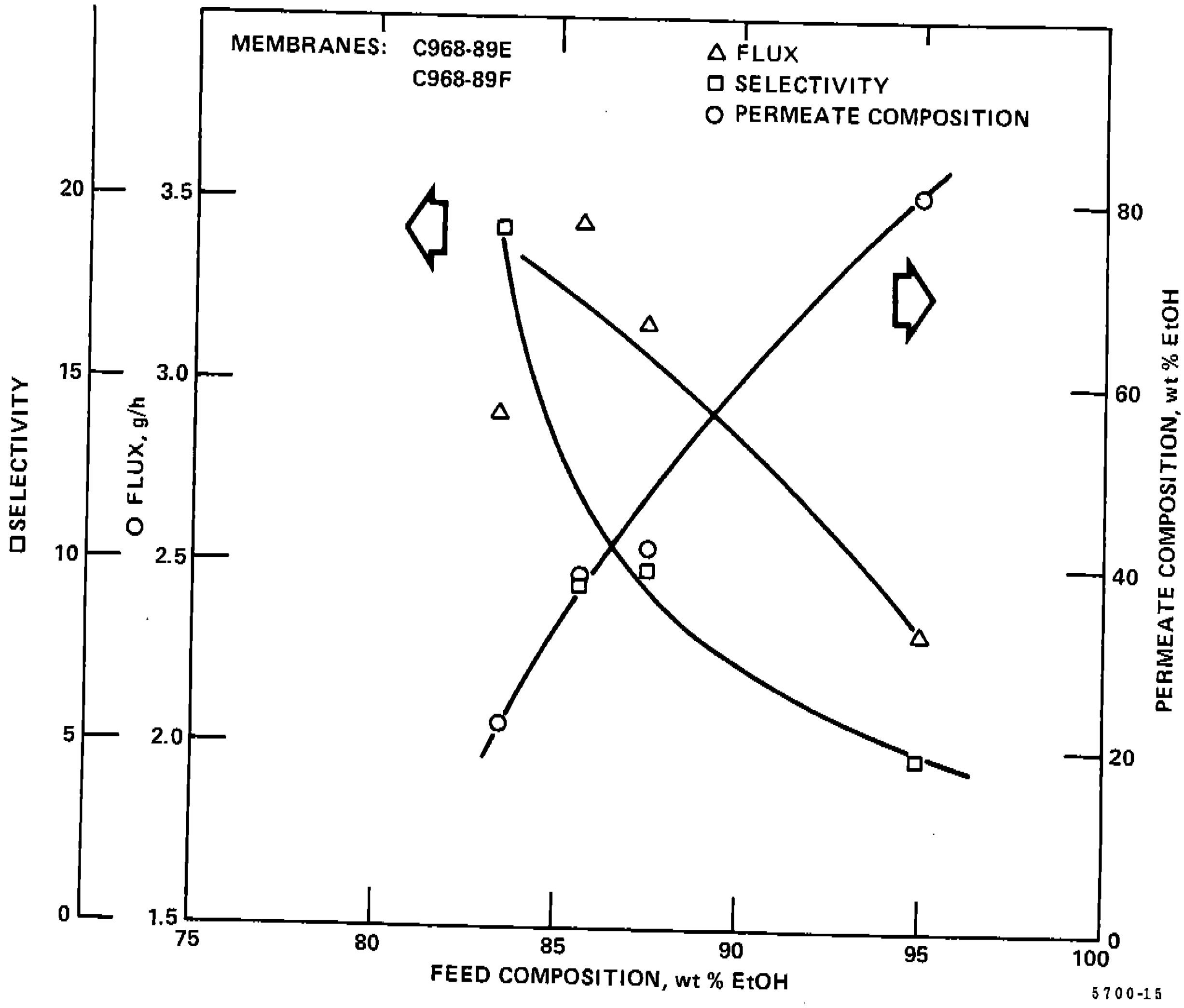

Figure 11. Average experimental data for two cellulose acetate membranes expressed as a function of feed composition.

not evaluate these membranes at higher feed concentrations, it is unknown whether cellulose acetate membranes exhibit permeatropism at 45° C, but the trend of the selectivity curve would indicate that permeatropism is not a factor for cellulose acetate membranes at this temperature. Hoover and Hwang (14) published results for ethanol-water separations using silicone-rubber membranes that showed the value for selectivity approaches but does not pass through the value of 1; therefore, no permeatropism exists. Other results (7) for polyetherurea membranes show that the separation factor equals one near the middle of the concentration range. However, for the ethanol-water system, most published data show that permeatropism occurs only at high ethanol concentrations.

When all of the data presented in Tables 8 and 9 were evaluated, we concluded that grafting of HEMA onto the surface of cellulose acetate menbranes had no positive effect on selectivity. It should be noted that some of the membranes did show an improvement in selectivity; however, this improvement was not shown consistently in other membranes grafted using the same procedure under similar conditions. The large deviations can be attributed in part to the oscillating trend shown by the experimental data.

V. CONCLUSIONS

Based on the results of our economic evaluation, we do not believe that ethanol-selective membranes hold much potential for reducing the capital and energy costs associated with the purification of fuel-grade ethanol from fermentation beers. Very large membrane areas are required even in cases where hypothetical membranes exhibiting much better performance than existing membranes are considered. Moreover, the membrane areas increase exponentially as the ethanol content of the waste stream is reduced to low levels. Although pervaporation does reduce the direct energy requirements for the separation, the ethanol content of the waste stream from pervaporation is high compared to the ethanol content of the waste stream from a conventional beer still. This lost ethanol represents a significant energy loss in the overall process and, when considered in light of the large membrane areas, makes the process uneconomical.

The use of ethanol-selective membranes in the concentration range of 40 to 80 wt % ethanol may become economical if membranes with very high flux and selectivity can be developed. Improvements of at least two orders of magnitude in both the flux and selectivity will be required before this application will be feasible.

Our results show that water-selective membranes are useful in the final dehydration of ethanol. Also, the greatest benefit from improved flux and selectivity with respect to the overall cost and energy requirements for ethanol purification can be realized with water-selective membranes. For this reason, we recommend that future work be directed toward improving the performance of water-selective membranes.

The studies that we conducted with both ethanol- and water-selective membranes gave disappointing results. Throughout the project we observed significant oscillations in the flux and permeant compositions as we switched from one trap to the other in the pervaporation units. Despite these problems, we did show that the addition of water-sequestering agents to ethanol-selective membranes does improve the selectivity of the membranes toward ethanol. Our efforts toward the development of water-selective membranes did not yield any significant improvements. Although some improvement over the cellulose acetate substrate was achieved, it is difficult to assess the utility of this approach.

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